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(54) IMPROVEMENTS RELATING TO THE PURIFICATION OF NITRILES

(71) I, MICHAEL W. PREUVENEERS, Chartered Patent Agent, of British nationality and of Britannic House, Moor Lane, London, E.C.2, do hereby declare the invention, which has been communicated to by UGINE KUHLMANN, of 10 Rue du General-Foy, Paris (VIII) France, a body corporate organised under the Laws of France, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method for purifying organic nitriles which have already been isolated and result from treatments of reaction mixtures obtained by catalytic reaction in the vapour phase of ethylenic hydrocarbons in the presence of ammonia and oxygen.

Although these nitriles have already been processed to a very large extent they still contain various impurities which whilst present in small quantities may still exert a great influence on the quality of the products subsequently manufactured from the nitrile monomers e.g. fibre grade polymer.

The elimination of these impurities which possess a weak basic character, particularly heterocyclic products containing one or more nitrogen atoms in the ring, such as substances with the azole, oxazole or iso-oxazole group, by distillation is theoretically possible but because of their volatility being very close to that of the nitriles, such a method of elimination would be very laborious and costly, particularly in the case of acrylonitrile.

It is an object of the present invention to provide an alternative method for eliminating these impurities.

Accordingly the present invention provides a process for the purification of nitriles produced by the vapour phase catalytic reaction of an olefin, oxygen and ammonia by the removal of basic heterocyclic compounds containing one or more nitrogen atoms in the ring which comprises contacting the nitrile with an activated adsorbent selected from

among alumina silica and certain decolourising clays belonging to the family of attapulgites, sepiolites or montmorillonites, or a mixture of these substances.

The activation is generally obtained by a thermal treatment for example heating the adsorbent in a molecular oxygen containing gas at temperatures of 150—350°C. Numerous commercial adsorbents may be used. When using alumina the adsorbent is preferably prepared from hydrogillite, gibbsite, of boehmite, which is dehydrated whilst being scavenged with a dry and inert gas so that, starting from ambient temperature, the temperature is raised to between 200 and 350°C, preferably in the vicinity of 300°C, in approximately 60 minutes. This temperature is maintained for several hours, preferably for 3—6 hours, and is followed by rapid cooling, still maintaining the alumina under a gaseous scavenging. The substance(s) is then kept in a moisture free atmosphere.

When using silica the adsorbent is preferably silica gel which is prepared by precipitating the silica from an aqueous solution of an alkali metal silicate, for example sodium meta-silicate, by the action of an acid such as concentrated hydrochloric acid. The precipitated silica gel is washed copiously with water on the filter and then dried. The dried mass is then divided into coarse grains of approximate size 0.1 to 2 mm, and then placed in a stove for 10 hours at a temperature of between 90 and 150°C, and preferably in the vicinity of 110°C. After cooling the product is screened.

When using decolourising clays, which are hydrated aluminium silicates whose composition may vary according to whether a part of the aluminium has been replaced in the molecule by magnesium or calcium, the treatment comprises as in the case of alumina, of heating up to a temperature of between 200 and 350°C and preferably in the vicinity of 300°C in about 60 minutes. This thermal treatment is applied over a period of 3 to 6 hours and is followed by rapid cooling. Among the substances of this type which

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are commercially available one may mention certain discolouring earths marketed by the French Company Carbonisation Et Charbons Actifs (C.E.C.A.S.A.), sold for example under the trade names of CLARSIL PC 1, LE 2, LER 49, LC and PC.

The treatment of the nitriles to be purified by adsorbents activated in this way may be carried out in a number of different ways.

Thus for example the product to be purified may be passed through a bed of adsorbent substance or be intimately mixed with the adsorbent substance, followed by filtration.

The adsorbent substances used in the method of the invention are capable of a long period of service, depending upon the quantities of impurities contained in the product to be purified and retained by the adsorbent. The quantities of impurities thus retained depend on numerous parameters such as temperature, particles size and rate of percolation if this particular method is employed.

The treatment may be carried out at various temperatures, but in order to avoid breakdown reactions of the nitriles which may occur at elevated temperatures, it is preferable to operate at ambient temperature or at lower temperatures. This recommendation also generally satisfies the laws of adsorption, since this is usually an exothermic phenomenon.

It is desirable to use a fine particle size adsorbent, the adsorption equilibria thus being reached more rapidly.

If a percolation method is employed it is preferable to use a low rate of flow, although this rate must be greater than the speed of diffusion.

When the amount of impurities retained by the adsorbent is judged sufficient, it is necessary to regenerate it. This may be done in the following manner; the adsorbent is washed with water, the volume of water used being between 50 and 100 times the volume of adsorbent used, and preferably in the vicinity of 80 times. After this washing the adsorbent is allowed to drain, is dried and is reactivated by heating.

The method according to the invention is illustrated by the following examples in which monomeric acrylonitrile manufactured from propylene, ammonia and air by vapour phase catalytic reactions and containing 85 ppm (parts per million) by weight of oxazole and 0.3% by water was employed. Oxazole is an impurity which it is difficult to eliminate by distillation. Its content in the products was determined by chromatography in the gaseous phase using an apparatus equipped with a very sensitive flame ionisation detector and already giving a significant response for an oxazole content of the order of 0.5 ppm.

EXAMPLE 1

The installation used consisted of a glass

tube with an internal diameter of 10 mm, a height of 500 mm, containing the adsorbent.

A plug of glass wool placed in the base of the tube prevents the adsorbent from being carried out of the tube. The product to be purified is fed by means of a dosing pump from a reservoir.

It is circulated through the adsorbent in a downwards direction, but an upward flow is also possible. At the top of the column a set of cocks which makes it possible to isolate the column or to replace the feed of product to be purified by a feed of water.

In the lower part of the column is also a set of cocks which makes it possible to direct the effluent product to receiver flasks, or a stream of liquid (water or nitrile) in the upwards direction so as to release the adsorbent where necessary or so as to wash it prior to reactivation.

The adsorption columns may be removed and placed in a cylindrical electric furnace for activation. The latter is carried out whilst scavenging with air, one of the ends of the adsorption column being connected to a compressed air pipe via a ground glass connection and a regulating valve.

As adsorbent 17 g of alumina is used prepared as described above and having a particle size of 200—500 μ , with an apparent density of 0.7. The adsorption column packed with the alumina is placed in the electric furnace and with a stream of air of a few litres per hour, approximately 10 litres passing through the alumina, the temperature of the furnace is raised to 300°C in one hour; the temperature is maintained, with the flow of air for 6 hours. The tube is then cooled and is assembled with the remaining apparatus.

Acrylonitrile containing 85 ppm of oxazole is passed down the column at a rate of approximately 500 mols of acrylonitrile flow per hour. It is arranged so that the bed of alumina operates whilst flooded.

Each fraction of 10 mls of acrylonitrile flowing out of the column is analysed by gas chromatography. Up to 245 mls no trace of oxazole is detected in the effluent; at 255 mls approximately 10 ppm of oxazole is detected. The break-through figure for the alumina is therefore in the vicinity of 250 mls, which represents a retention of 1.0 g of oxazole per kg of alumina.

The operation is continued until the concentration of oxazole in the effluent acrylonitrile has reached the oxazole concentration of the in-flowing acrylonitrile, that is to say 85 ppm. This takes place at about 350 mls of acrylonitrile.

The alumina is then totally saturated with oxazole. The operation is then stopped and the acrylonitrile.

In industrial practice it will be appreciated

that in this way 1 ton of oxazole-free acrylonitrile can be obtained by treating 1 ton of acrylonitrile with 85 ppm of oxazole over 85 kg of alumina, which can be regenerated.

EXAMPLE 2

This example relates to the regeneration of the alumina used in Example 1.

For this purpose water is circulated upwards through the adsorption column, at a rate of approximately 1.9 litres in 1 hour.

The alumina is drained. The adsorption column is placed in an electric furnace and the adsorbent is heated to 300°C whilst scavenging with air at a flow rate of about 10 litres per hour, the time required for the temperature to rise to 300°C being 1 hour. The temperature is maintained at 300°C for 5 hours and the column and adsorbent thereafter cooled.

Repeating the experiment as described in Example 1 using the regenerated adsorbent, a fresh quantity of 250 mls free from oxazole is obtained from acrylonitrile containing 85 ppm of oxazole.

The same batch of alumina may be regenerated many times, which decreases in the same proportion the consumption of alumina per ton of purified product.

EXAMPLE 3

To 1,000 mls of acrylonitrile containing 85 ppm of oxazole is added 40 g of CLARSIL* PC 1 which is a decolourising earth in powder form and has previously been activated by heating for 5 hours at 300°C.

The suspension is agitated at ordinary temperature for 15 minutes. It is then filtered. The filtrate is analysed and it is found that the acrylonitrile thus treated does not contain more than 34 ppm of oxazole. This means that 60% of the oxazole containing originally by the acrylonitrile has been eliminated.

The solid retained on the filter is washed with 50 mls of water in several fractions. The solid is dried and placed in a furnace with a circulation of air. After 5 hours at 300°C it is cooled and it is found by treating a further sample of acrylonitrile containing oxazole that the initial purification efficiency has been regained.

*Regd. Trade Mark.

EXAMPLE 4

Example 3 is repeated making use of different decolourising earths on the basis of 5 parts by weight of decolourising earth per 100 parts by weight of acrylonitrile and agitating for 15 minutes at ordinary temperature.

The results obtained are shown in the table below.

The purification efficiency "R" is understood to mean the following ratio

$$\frac{(\text{initial concentration of oxazole} - \text{final concentration})}{\text{initial concentration}} \times 100 \quad 65$$

		R	
CLARSIL LE 2	...	50%	
CLARSIL LER 49	...	62	
CLARSIL LC	...	54	
CLARSIL PC	...	50	70
CLARSIL PCS	...	12	

All these decolourising earths were washed with water after use and then reactivated as described in Example 3. After reactivation the initial properties were found to be restored.

EXAMPLE 5

200 mls of sodium silicate containing 500 g per litre, to which 1500 mls of water had been added were treated with concentrated hydrochloric acid so as to give an acid medium. The silica is precipitated and is filtered and the precipitate washed with water until the washing waters have a pH of 6.5-7. The silica gel is then dried in the stove at 110°C overnight. It is then ground and the fraction with a particle size of between 0.210 mm and 0.420 mm retained by screening. 8.726 g of activated silica thus obtained above are placed in the apparatus described in Example 1 above.

Acrylonitrile containing 85 ppm of oxazole are percolated through the silica contained in the column and each fraction of 25 mls which flows out of the column is analysed.

After 225 mls have percolated through at a speed of 250 mls per hour, the concentration of oxazole in the effluent acrylonitrile corresponds to that in the acrylonitrile which was fed in.

0.45 g of oxazole has been retained per kg of silica gel.

The silica gel is washed with 50 mls of water; then it is dried and heated at 110° for 10 hours to restore the original properties.

WHAT I CLAIM IS:—

1. A process for the purification of nitriles produced by the vapour phase catalytic reaction of an olefin, oxygen and ammonia by the removal of basic heterocyclic compounds containing one or more nitrogen atoms in the ring which comprises contacting the nitrile with an activated adsorbent selected from alumina, silica, attapulgite, sepiolite, or montmorillonite.

2. A process as claimed in claim 1 wherein the adsorbent is activated by heating in a molecular oxygen containing gas at temperatures of 150—350°C. 25
- 5 3. A process as claimed in claim 1 or 2 wherein the adsorbent is alumina prepared by the dehydration of hydrogillite, gibbsite or boehmite whilst being scavenged with a dry inert gas and the temperature raised from ambient to between 200 and 350°C in about 60 minutes, maintaining at the elevated temperature for from 3 to 6 hours and thereafter rapidly cooling. 30
- 10 4. A process as claimed in claim 1 or 2 wherein the adsorbent is silica prepared by precipitation from an aqueous solution of an alkali metal silicate by the addition of acid followed by washing and drying the precipitate, dividing into coarse grains of approximate size 0.1 to 2 mm and heating it for about 10 hours at a temperature of between 90 and 150°C and thereafter rapidly cooling it and screening the cooled product. 35
- 15 5. A process as claimed in claims 1 or 2 wherein the adsorbent is attapulgite, sepiolite or montmorillonite which is activated by heating from ambient temperature up to between 200 and 350°C in about 60 minutes maintaining at the elevated temperature for from 3 to 6 hours and thereafter rapidly cooling. 40
- 20 6. A process as claimed in any one of the preceding claims carried out by passing the nitrile to be purified through a packed bed of adsorbent. 45
7. A process as claimed in any one of claims 1 to 5 carried out by slurring the nitrile to be purified with the adsorbent and recovering the pure nitrile by filtration.
8. A process for the purification of nitriles as claimed in claim 1 substantially as hereinafter described with reference to the examples.
9. Acrylonitrile wherever purified by a process according to any one of the preceding claims.
- MICHAEL W. PREUVENEERS,
Agent for the Applicants.

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